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XVII.

ON DIAMIDO-SULPHOBENZIDE-DICARBONIC ACID.

By Arthur Michael and T. H. Norton.

Presented by E. N. Horsford, May 9th, 1877.

Of the large number of amido-sulpho-benzoic acids which are possible according to our present theories, but three have been obtained thus far. Two of these were prepared by Griess,* from the action of sulphuric acid on meta-amido-benzoic acid. Limpricht and Uslar † obtained the third by reduction of the mono-nitro derivative of meta-sulpho-benzoic acid. It seemed therefore of interest to us to study the action of sulphuric acid on ortho-amido-benzoic acid and para-amido-benzoic acids, not merely in order to increase the list of isomeric amido-sulpho-benzoic acids, but because of the possibility that, by removal of the amido group, the as yet unknown ortho-sulpho-benzoic acid could be obtained.

Our experiments were first directed to para-amido-benzoic acid; and here an unexpected character was assumed by the reaction, the results of which we briefly communicate.

We prepared the para-amido-benzoic acid for our purpose from the solid para-nitro-toluol, by oxidation and subsequent reduction of the nitro group. In the former operation it was observed that much better results were obtained from treatment with potassium permanganate, than from the methods hitherto used for this body, viz., with nitric acid or potassium bichromate and sulphuric acid. The best proportions were found to be 2½ mol. $KMnO_4$ to 1 mol. $C_6H_4(NO_2)(CH_3)$ in a solution of 40 parts water to 1 part $KMnO_4$. The reduction was effected by means of tin and hydrochloric acid, in proportions 1 part $C_6H_4(NO_2)(COOH)$ to 2.15 parts Sn. In order to remove the excess of hydrochloric acid previous to the precipitation of the tin, the solution is evaporated on the water-bath to dryness. The temperature should not, however, go beyond this point, as we had opportunity to observe that even at 100° small quantities of aniline were formed, while at 120° the para-amido-benzoic acid was decomposed completely into carbonic acid and aniline. It would be of interest to examine the action of $SnCl_2$ on other aromatic acids under the conditions mentioned. The solution of para-amido-benzoic acid was treated with sodium carbonate, and the acid precipitated out by means of acetic acid. After a single crystallization in water, it showed the melting point 186°.

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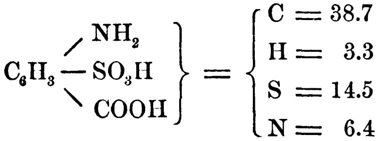
* Jour. f. prakt. Chemie [2], 5, 244.

† Ann. Chem. Pharm., 106, 29.

The para-amido-benzoic acid obtained in this way was placed in a flask, and a sufficient quantity of slightly fuming sulphuric acid (s. g. 1.850) added to dissolve the mass. The flask was then exposed to a temperature of 170° — 190°, for from three to four hours, in a paraffine bath. After cooling, the contents of the flask were removed by means of water, and barium-carbonate was added to the solution until it was neutralized. The liquid was boiled for several hours, and then filtered. It was necessary to heat the residue repeatedly with hot water before a slight pinkish hue could be removed. Exactly enough sulphuric acid was added to the filtrate to precipitate the barium, and it was separated from the barium sulphate formed. By the evaporation of this solution, groups of crystals separated out, showing various shades of yellow, orange, and red. Several crystallizations from water freed them from small quantities of a by-product consisting of minute red crystals, and after boiling with animal charcoal they retained a faint pink color. The substance was dried at 110°, and submitted to a series of analyses. The sulphonic acid which was expected as the natural result of the reaction, would have yielded the following percentages: —



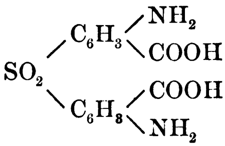
$$\left.C_6H_3\begin{array}{l} / NH_2 \\ - SO_3H \\ \backslash\ COOH \end{array}\right\} = \begin{cases} C = 38.7 \\ H = 3.3 \\ S = 14.5 \\ N = 6.4 \end{cases}$$

The analyses showed, however, that we had obtained a body of an entirely different nature, and led to the following formula: —

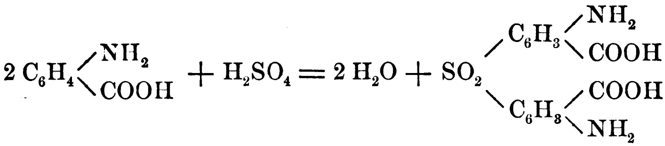
$$C_{14}H_{12}N_2SO_6.$$

	Calculated.	Found (mean).
C =	50.00	50.18
H =	3.57	4.20
N =	8.26	8.06
S =	9.60	10.10
O =	28.57	
	100.00	

This formula would naturally be resolved into the structural formula,



or diamido-sulphobenzide-dicarbonic acid, the reaction being as follows: —



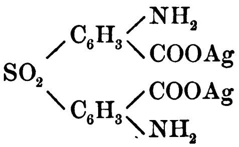
The melting point of the acid is above 350°. It is easily soluble in hot water, and on cooling separates out in groups of fern-shaped crystals. It is much less soluble in alcohol and ether, their addition to the aqueous solution causing the precipitation of the acid in a white, flocculent mass; chloroform dissolves it with difficulty; while it is almost entirely insoluble in carbon bisulphide and benzine. Sulphuric acid dissolves it easily, forming a compound which is precipitated on the addition of alcohol, and is extremely soluble in water. This compound awaits farther investigation. In concentrated hydrochloric acid it is completely insoluble. It dissolves easily in warm nitric acid, but cannot be precipitated by the addition of alcohol.

The new compound exhibits strongly marked acid properties, and dissolves easily in alkalies. The neutral solution in ammonia yields on evaporation the ammonium salt, in handsome laminated crystals, which are easily soluble.

The potassium salt obtained in the same way consists of small, fine, colorless needles.

The lead salt is white, and nearly insoluble in water.

The silver salt precipitated from the solution of the ammonium salt by the addition of nitrate of silver, is obtained in the form of small, white laminæ, which are tolerably insoluble in water, and gradually assume a brown color on exposure to the sunlight. The analysis of this salt coincided closely with the formula



$$SO_2\left\langle\begin{array}{l}C_6H_3\left\langle\begin{array}{l}NH_2\\COOAg\end{array}\right.\\C_6H_3\left\langle\begin{array}{l}COOAg\\NH_2\end{array}\right.\end{array}\right.$$

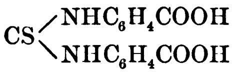
Calculated.	Found.
$Ag = 37.45$	37.62

The barium salt is extremely soluble, and not adapted for analysis.

The reaction of para-amido-benzoic acid, just described, recalls the analogous reaction of phenol with sulphuric acid. Glutzt* and Annaheim † have shown that, if an excess of sulphuric acid be avoided, oxysulpho-benzide is obtained with great ease. As in the case of oxysulpho-benzide and all members of the sulphine group, our compound should also pass over into the corresponding sulphonic acid, by increasing the amount of sulphuric acid used.

Unfortunately we are compelled temporarily to interrupt the investigation, but hope at an early date to be able to communicate farther experiments in the direction mentioned.

Merz and Weith ‡ obtained several years since a dicarboxyl-sulphcarbanilid,



$$CS\left\langle\begin{array}{l}NHC_6H_4COOH\\NHC_6H_4COOH\end{array}\right.$$

a well-defined crystalline compound, by the action of carbon disulphide on metamido-benzoic acid. We have sought to prepare the corresponding derivative of para-amido-benzoic acid, but so far without success. The alcoholic solution of carbon disulphide and para-amido-benzoic acid was heated in an open flask and in sealed tubes at various temperatures. In all cases we obtained a yellow, resinous mass, from which no well-characterized compound could be separated.

Berlin, Universitäts-Laboratorium, April, 1877.

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* Ann. Chem. Pharm., 147, 52.

† Ann. Chem. Pharm., 172, 28.

‡ Ber. Deutsch. Chem. Gesell., 3, 812.